

Reviewed by: SanYvette Williams, D.V.M. *WWS 9/26/91*
Section IV, Tox. Branch II (H7509C)
Secondary Reviewer: Elizabeth Doyle, Ph.D. *E.A. Doyle 9/27/91*
Section IV, Tox. Branch II (H7509C)

DATA EVALUATION REPORT

STUDY TYPE: Leaching (#163-1)

TOX. CHEM. NO.: 129057

HED NO.: 1-0266

TEST COMPOUND: Silver Copper Zeolite

ACCESSION NO.: 416158-18

ADL REFERENCE NO.: 63614-04

TITLE OF REPORT: Silver Copper Zeolite: Leaching of Silver and Copper from
Impregnated Polymers

AUTHOR: Judith C. Harris, Ph.D.

DATE: Aug. 3, 1990

SPONSOR: Kanebo Zeolite USA, Inc.

PERFORMING LAB: Arthur D. Little, Inc.; Acorn Park, Cambridge, MA 02140

CONCLUSIONS: The maximum concentrations of metals in the aqueous leachate after
correction for silver recovery were:

Material	Silver (ug/L)	Copper (ug/L)
Polyester/Cotton	16	210
Non-woven Polyester	35	345
Polypropylene Plate	8.9	9.3

-The concentrations of silver and copper in the leachates generated in this study are below U.S.EPA drinking water guideline (50 ug/L) for silver and the ambient water quality criterion (1000 ug/L) for copper.

This study does not conform to guidelines for a leaching study (#163-1). Leaching should also be performed at neutral and basic pH's in order to mimic effects of body fluid, toiletries or laundry products. This study is classified supplementary.

CLASSIFICATION: Core - supplementary.

GLP COMPLIANCE: Statement included on page 3 of study.

QUALITY ASSURANCE: Statement included on page 7 of report.

BACKGROUND: This study was performed "to determine the quantity of soluble silver and copper released into an aqueous medium from polymeric materials impregnated with silver copper zeolite".

A. MATERIALS:

Test material: Silver copper zeolite contained 3.4% silver and 6.1% copper on a dry weight basis. Zeolite was incorporated into three polymer matrices listed below:

Material PE -- Polyester Non-woven Fabric (E-1)
Polyethylene terephthalate staple fiber incorporated with silver copper Zeolite at 1.5% by weight by mixer kneading. Non-woven production: carding and needle punching.

Material PC -- Polyester/Cotton Woven sheeting (E-2)
Polyethylene terephthalate staple fiber incorporated with silver copper zeolite at 1.5% by weight by mixer kneading. Polyester fiber blended with cotton (no zeolite) at 1:1 by weight. Sheeting production: polyester and cotton blending. Fiber opening: carding, drafting, yarn spinning, weaving, scouring, bleaching, dyeing and drying.

Material PP -- Polypropylene plate (E-3)
Polypropylene plate of polypropylene incorporated silver copper zeolite at 1.5% by weight by extruder kneading. Plate preparation by injection molding.

Negative controls: Consisted of vials containing 30 mL leaching medium (ASTM Type I water), nichrome wire, and glass beads, but no polymeric material test coupons.

Positive controls: Same as negative controls along with a small volume of a standard solution containing silver and copper ions to give an initial concentration of 5 ppb(ug/L) of silver and 25 ppb (ug/l) of copper.

Test Exposure System:

This system was designed to allow control of light, temperature and agitation of the test vial's contents. The test was conducted inside a black exposure chamber that had air vents permanently shielded and the top in place except when samples were removed. Temperature was controlled by a circulating water bath set at $25 \pm 0.1^{\circ}\text{C}$. The content of the vial was mechanically agitated using a magnetic stir plate.

B. STUDY DESIGN:

Test coupons of the polyester/cotton sheeting (E-2) and non-woven polyester (E-1) were cut as 1.7 cm x 1.7 cm (± 0.1 cm) squares. The coupons were individually weighed and then strung in groups of three onto nichrome wire with glass bead spacers.

Test coupons of the polypropylene plate material (E-3) were cut (1.5 cm x 1.5 cm) into squares, weighed and then strung into groups of three onto nichrome wire with glass bead spacers.

The coupon assemblies were placed into individual 40-mL glass vials that had been pre-cleaned by rinsing with 10% nitric acid followed by ASTM Type I water. A magnetic stirrer was in each vial. The leaching medium (30 mL ASTM Type I water) was added to each vial. The initial pH of the medium in each vial was measured and recorded using narrow-range pH paper.

After the vials were placed in the constant temperature water bath, taken as time zero (t_0), samples were withdrawn at intervals of 1, 2, 4, 8 and 15 days (± 1 hour), after time zero, for subsequent chemical analysis. The pH was again measured, then a measured quantity of concentrated nitric acid was added to bring the pH below 2. The vials were then stored in the dark in a 4 °C refrigerator before analysis.

Chemical analysis and data reduction:

Graphite Furnace Atomic Absorption Spectroscopy (GFAA) was used to analyze samples of the leachate, negative and positive controls. An external calibration curve based on freshly prepared standards was generated to help in quantification. Samples and calibration standards were filtered prior to analysis. Leachate samples were diluted to bring instrumentation response within the documented linear range of the analysis.

Calibration curves and calculated sample concentrations were based on the average height of the GFAA peak for two sequential analyses of each sample or diluted sample.

C. RESULTS:

Results of leaching tests for negative controls (Table 1 appended):

According to protocol, the data quality objective for the negative controls should be $<5X$ the Level of Quantification (LOQ) for silver and $<1X$ LOQ for copper. After the calibration standards were measured, the analytical LOQ was determined to be 0.15 ppb for silver and 4.0 ppb for copper. Therefore, all negative controls in this study had concentrations below the LOQ.

Results of leaching tests for positive controls (Table 2 appended):

The analysis of positive controls, which were spiked with 5 ppb (ug/L) silver and 25 ppb (ug/L) copper, show that the percent of copper recovered was met or just a little less than the protocol objective of 85 to 115% (avg.: 85%). There was a low recovery rate for silver (avg: 11%), however. It was thought by the registrant to be due to irreversible adsorption of silver onto the glassware (This theory was supported by the results of a previous pH 7 hydrolysis study). By assuming that a constant amount of silver had been lost from each study test vial, the practical lower limit of detection would increase from the analytical value of 0.15 ppb to 6.2 ppb (0.187 ug/0.030 L). Quality control results also suggest that 6.2 ppb should be added to the measured silver concentration for each leachate sample to compensate for possible irreversible adsorption within each test vial.

Results of tests for polyester/cotton material (Tables 4-7 appended):

The estimate of uncertainty in area (Table 4) is consistent with the variability in the measured total coupon weights, which average 50.6 mg ($\pm 15\%$ relative standard deviation).

The pH values (Table 5) measured on each test date were those expected for ASTM Type I water, even though initial pH values were low (avg. 5.0). Analysis of duplicate aliquots from the same vial meet the data quality objective (DQO, $\pm 10\%$ range percent difference (RPD)) stated in the protocol.

Measured concentrations of silver were corrected for low recovery, but the measured copper concentrations were used without correction, since the recovery of copper from the positive control samples was good.

Data presented in Tables 6 & 7 show that there is no strong correlation between the time of exposure and the amount of copper and silver leached.

Results of Leaching Tests for Non-Woven Polyester Material (Table 8, 10 & 11 appended):

This estimate of uncertainty in area is consistent with the variability in the measured total coupon weights, which average 128 mg ($\pm 14\%$ relative standard deviation).

Since 30 mL of leaching medium was added to each vial, the ratio of leachate to non-woven polyester material was approximately 0.23 mL/mg and 1.8 mL/cm².

Results for the analysis of duplicate aliquots of sample (PE-8) meet the protocol DQO of $\pm 10\%$ RSD for both silver and copper analyses performed on a single day. An increase in RSD to $\pm 16\%$ is observed when data from 2 days are pooled. Other samples analyzed on both days show RSDs ranging from 5 to 31%.

Results of silver (corrected concentrations) and copper leachate data (Tables 10 & 11) show no clear correlation between the time of exposure (0-15 days) and the quantity of silver and copper leached.

Results of Leaching Tests for Polypropylene Plate Material (Tables 10 & 11 appended):

The measured concentrations of silver and copper were below the level of quantification (0.15 and 4 ppb for silver and copper, respectively). Maximum leached quantities on a unit weight/unit area basis for silver (corrected for recovery) and copper are calculated as:

Silver
0.15 ug/g \rightarrow 0.014 ug/cm²

Copper
0.16 ug/g \rightarrow 0.015/cm²

Discussion\Conclusion:

-It should be noted that the registrant conducted pH analyses in the acidic range. Before an accurate assessment of leachability can be made, there should

be analyses made at the neutral and basic ranges.

-The results of this study show no clear time-dependence (over a 15-day period) of the leachability of silver and copper from polymers impregnated with silver copper zeolite.

-The results of positive controls indicate that irreversible losses of silver occurred; this resulted in a practical level of detection for silver of about 6.2 ppb compared to the analytical detection limit of 0.15 ppb.

-The range of quantities of silver (after correction for recovery) and copper (ug/g of polymer) released under conditions of the study were:

Material	Silver (ug/L)	Copper (ug/L)
Polyester/Cotton	4.2 - 12.3	47 - 137
Non-woven Polyester	5.5 - 8.2	46 - 75
Polypropylene Plate	ND - 0.15	ND - 0.16

-The maximum concentrations of metals in the aqueous leachate after correction for silver recovery were:

Material	Silver (ug/L)	Copper (ug/L)
Polyester/Cotton	16	210
Non-woven Polyester	35	345
Polypropylene Plate	8.9	9.3

-The concentrations of silver and copper in the leachates generated in this study are below U.S.EPA drinking water guideline (50 ug/L) for silver and the ambient water quality criterion (1000 ug/L) for copper.

This study does not conform to guidelines for a leaching study (#163-1). Leaching should also be performed at neutral and basic pH's in order to mimic effects of body fluid, toiletries or laundry products. This study is classified core - supplementary.

Table 1: Results for Leaching Study Blank Samples

BLANK	TEST DAY	AG,PPB	CU,PPB
B-8	0	<0.15 (0.066)	<4.0 (ND)*
B-1	1	<0.15 (0.046)	<4.0 (ND)
B-2	2	<0.15 (0.048)	<4.0 (0.85)
B-3	4	<0.15 (0.056)	<4.0 (ND)
B-4	8	<0.15 (0.064)	<4.0 (ND)
B-7 (REP)	8	<0.15 (0.068)	<4.0 (ND)
B-5	15	<0.15 (0.092)	<4.0 (ND)

* ND = Not detected; response in laboratory blank range

Table 2: Results for Analysis of Leaching Study Positive Controls

Spike level = 5 ppb silver, 25 ppb copper

SAMPLE	TEST DAY	-----SILVER-----			-----COPPER-----		
		FOUND ug/L	% RECOVERY	LOSS ug	FOUND ug/L	% RECOVERY	LOSS ug
C-8	0	1.1	22	0.117	21	84	0.120
C-1	1	0.24	5	0.143	22	88	0.090
C-2	2	<0.15 (0.09)	2	0.150	22	88	0.090
C-3	4	<0.15 (0.12)	2	0.150	21	84	0.120
C-3 (DUP)*	4	<0.15 (0.09)	2	0.150	20	80	0.150
C-4	8	2.5	51	0.075	21	84	0.120
C-5	15	<0.15 (0.10)	2	0.150	23	84	0.120
C-7 (REP)*	15	<0.15 (0.07)	1	0.150	22	88	0.090
AVERAGE			11	0.134		85	0.112

* DUP = Analysis of replicate aliquot from same vial

REP = Analysis of replicate vial

Table 4: Coupon Weights and Areas for Polyester/Cotton Leaching Tests

	COUPON WEIGHT (mg)			COUPON AREA (cm ²)*	
SAMPLE	#1	#2	#3	TOTAL	TOTAL
PC-1	13.1	13.2	12.3	38.6	17
PC-2	12.4	24.2	19.5	56.1	17
PC-3	13.2	20.7	19.3	53.2	17
PC-4	18.9	16.8	23.4	59.1	17
PC-5	12.8	13.0	13.6	39.4	17
PC-6	12.6	18.2	20.3	51.1	17
PC-7	19.9	14.4	19.8	54.1	17
PC-8	12.5	21.1	19.9	53.5	17

* 3 Coupons x 2 sides x 1.7 cm x 1.7 cm

$$\frac{X \mu\text{g Ag or Cu}}{0.0386\text{g cloth}} = \frac{Y \mu\text{g}}{75\text{g}}$$

Table 5: Silver and Copper Concentration Data for Polyester/Cotton Leachates

SAMPLE	INIT pH	TEST DAY	TEST DATE	FINAL pH	ASSAY DATE	SILVER		COPPER	
						PPB (MEAS)	RPD (%)	PPB	RPD (%)
PC-8	5.0	0	May 3	6.8	May 18	3.1		84	
PC-1	5.0	1	May 4	6.0	May 18	4.6	2.2	161	8.4
PC-1 (DUP)*	5.0	1	May 4	6.0	May 18	4.7		148	
PC-2	5.0	2	May 5	6.8	May 18	9.6	134	178	59
PC-7 (REP)*	5.0	2	May 5	6.5	May 18	1.9		97	
PC-3	5.0	4	May 7	6.5	May 18	5.6		211	
PC-4	5.0	8	May 11	6.5	May 18	2.1		116	
PC-5	4.5	15	May 18	6.0	May 21	10.0		180	

* (DUP) = analysis of a replicate aliquot from the same vial
 (REP) = analysis of a replicate vial

00.0 5.2
 PCO
 147

0.00
 < 10%
 > 120%

Table 6: Silver Leached from Polyester/Cotton Material on a Unit Weight/Area Basis

SAMPLE	TEST DAY	SILVER				
		ppb (meas)	ppb (corr) **	ug/g ✓	ug/cm2	% of Total ***
PC-8	0	3.1	9.3	5.2	0.016	2.0
PC-1	1	4.6	10.8	8.4 ✓	0.019	3.3
PC-1 (DUP)*	1	4.7	10.9	8.5 ✓	0.019	3.3
PC-2	2	9.6	15.8	8.9 ✓	0.028	3.5
PC-7 (REP)*	2	1.9	8.1	4.5 ✓	0.014	1.8
PC-3	4	5.6	11.8	6.7 ✓	0.021	2.6
PC-4	8	2.1	8.3	4.2	0.015	1.7
PC-5	15	10.0	16.2	12.3	0.029	4.8
RANGE				4.2-12.3	0.014-0.029	1.7-4.8
MEAN				7.3	0.020	2.9
STANDARD DEVIATION				2.7	0.0055	1.1
RELATIVE STANDARD DEVIATION, %				37	27	38

* DUP = Analysis of replicate aliquot from same vial
 REP = Analysis of replicate vial

** Corrected for observed average loss of silver at pH 6-7,
 equivalent to 6.2 ppb.

*** Total Silver = Wt. of polymer x 1.5% zeolite by weight x 3.4% silver
 in zeolite x 0.5 (1:1 fiber blend; no zeolite in cotton)

Table 7: Copper Leached from Polyester/Cotton Material on a Unit Weight/Area Basis

*copper
from material*

SAMPLE	TEST DAY	COPPER			
		ppb	ug/g	ug/cm2	% of Total **
PC-8	0	84	47	0.15	10.3
PC-1	1	161	125 ✓	0.28	27.4
PC-1 (DUP)*	1	148	115 ✓	0.26	25.1
PC-2	2	178 ?	100 ?	0.31	21.9
PC-7 (REP)*	2	97	54 ✓	0.17	11.8
PC-3	4	211	119 ✓	0.37	26.0
PC-4	8	116	59	0.20	12.9
PC-5	15	180	137	0.32	30.0
RANGE			47-137	0.15-0.37	10.3-30
MEAN			95	0.26	21
STANDARD DEVIATION			36	0.078	7.8
RELATIVE STANDARD DEVIATION			38	30	38

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* DUP = Analysis of replicate aliquot from same vial
 REP = Analysis of replicate vial

** Total Copper = Wt. of polymer x 1.5% zeolite by weight x 6.1% copper
 in zeolite x 0.5 (1:1 fiber blend; no zeolite in cotton)

Table 8: Coupon Weights and Areas for Non-Woven Polyester Leaching Tests

SAMPLE	COUPON WEIGHT (mg)			COUPON AREA (cm2)*	
	#1	#2	#3	TOTAL	TOTAL
PE-1	41.9	37.5	51.2	131	17
PE-2	39.8	36.1	35.3	111	17
PE-3	49.3	32.5	36.5	118	17
PE-4	44.2	49.4	48.1	142	17
PE-5	43.9	51.3	42.4	138	17
PE-6	41.8	36.3	38.5	117	17
PE-7	42.8	35.9	37.3	116	17
PE-8	49.3	48.7	50.1	148	17

* 3 Coupons x 2 sides x 1.7 cm x 1.7 cm

Table 9: Silver and Copper Concentration Data for Non-Woven Polyester Leachates

SAMPLE	INIT pH	TEST DAY	TEST DATE	FINAL pH	ASSAY DATE	SILVER PPB (MEAS)	RPD or RSD %	COPPER PPB	RSD %
PE-8	5.5	0	May 3	6.5	May 18	32	16	222	5
PE-8 (DUP)*	5.5	0	May 3	6.5	May 21	25		**	
PE-8 (DUP)*	5.5	0	May 3	6.5	May 18	34		234	
PE-8 (DUP)*	5.5	0	May 3	6.5	May 21	25		**	
PE-1	5.0	1	May 4	6.5	May 18	15	32	168	44
PE-7 (REP)*	5.0	1	May 4	6.3	May 18	28		263	
PE-7 (DUP)*	5.0	1	May 4	6.3	May 21	19		**	
PE-2	4.5	2	May 5	6.8	May 18	26	17	249	
PE-2 (DUP)*	4.5	2	May 5	6.8	May 21	22		**	
PE-3	5.0	4	May 7	6.5	May 18	26	31	276	
PE-3 (DUP)*	5.0	4	May 7	6.5	May 21	19		**	
PE-4	5.5	8	May 11	6.0	May 18	20	5	256	
PE-4 (DUP)*	5.5	8	May 11	6.0	May 21	19		**	
PE-5	5.0	15	May 18	6.5	May 21	20		345	**

* (DUP) = analysis of a replicate aliquot from the same vial
 (REP) = analysis of a replicate vial

** Leachates analyzed on May 21 were at a 1:50 dilution.
 Copper was diluted down to the detection limit range.

Table 10: Silver Leached from Non-Woven Polyester Material on a Unit Weight/Area Basis

SAMPLE	TEST DAY	SILVER		ug/g	ug/cm2	% of Total ***
		ppb (meas)	ppb (corr) **			
PE-8 (ave)*	0	29	35	7.1	0.062	1.4
PE-1 (ave)*	1	21	27	6.2	0.047	1.2
PE-2 (ave)*	2	24	30	8.2	0.053	1.6
PE-3 (ave)*	4	23	29	7.3	0.051	1.4
PE-4 (ave)*	8	20	26	5.5	0.046	1.1
PE-5	15	20	26	5.6	0.045	1.1
RANGE				5.5-8.2	0.045-0.062	1.1-1.6
MEAN				6.6	0.051	1.3
STANDARD DEVIATION				1.1	0.006	0.21
RELATIVE STANDARD DEVIATION				16	12	16

* (ave) = Arithmetic Mean of Values in Table 9

** Corrected for average loss of silver at pH 6-7, equivalent to 6.2 ppb.

*** Total silver = weight of polymer x 1.5% zeolite by weight x 3.4% silver in zeolite

Table 11: Copper Leached from Non-Woven Polyester Material on a Unit Weight/Area Basis

SAMPLE	TEST DAY	COPPER			% of Total ***
		ppb	ug/g	ug/cm2	
PE-8 (ave)*	0	228	46	0.40	5.1
PE-1 (ave)*	1	216	49	0.37	5.4
PE-2 (ave)*	2	249	67	0.43	7.4
PE-3 (ave)*	4	276	70	0.48	7.7
PE-4 (ave)*	8	256	54	0.44	5.9
PE-5	15	345	75	0.60	8.2
RANGE			46-75	0.37-0.60	5.1-8.2
MEAN			60.4	0.45	6.6
STANDARD DEVIATION			12.0	0.08	1.3
RELATIVE STANDARD DEVIATION			20	18	20

* (ave) = Arithmetic Mean of Values in Table 9

*** Total copper = weight of polymer x 1.5% zeolite by weight x 6.1% copper in zeolite